Field Measurements of Seawater Inherent Optical Properties

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Abstract

The following measurement profiles are collected during the Biome-04 campaign. An AC-9 and an AC-S meters are deployed to measure the seawater absorption and attenuation. The back-scattering is measured with a BB-9 meter. Two WETStar fluorometers retrieve the Chlorophyll-*a* and the colored dissolved organic matter concentration. The photosynthetically active radiation is determined with a single channel PAR sensor. Seawater temperature and salinity are measured with a CTD device. All sensors are mounted on a single frame, called the IOP-frame. This chapter describes each measurement device, the related calibration and data processing. The structure of IOP-frame, the tubing configuration for the seawater sampling and the field measurements results are then presented.

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1 Introduction

The collection of seawater Inherent Optical Properties (IOPs) during the Biome-04 cruise is performed with a set of instruments mounted on a single frame, identified as the IOP-frame. The IOP-frame holds: *i.* devices for measuring seawater absorption and attenuation (AC-9 and AC-S), and back-scattering (ECO BB-9); *ii.* two WETStar fluorometers for retrieving the concentration of Chlorophyll-*a* (*Chl-a*) and Colored Dissolved Organic Matter (CDOM); *iii.* a single channel sensor for the Photosynthetically Active Radiation (PAR); and *iv.* a CTD meter for collecting temperature and salinity profiles.

The instrument set and the data acquisition system are described in Section 2. Section 3 presents the structure of the IOP-frame and the tubing configuration that collects the seawater for absorption, attenuation, *Chl-a* and CDOM measurements. Section 4 presents the experimental data. Results and future work plans are discussed in Section 5.

2 Instrument set

2.1 Attenuation and absorption (AC-9)

The IOP-frame is equipped with an AC-9 and an AC-S for measuring the seawater spectral absorption, a, and attenuation, c. These meters are manufactured by WETLabs, 620 Applegate St. Philomath, OR 97370, USA. This Section presents the AC-9 meter.

The AC-9 measures a and c at nine wavelengths. Measurements are taken flushing the water sample through two tubes with a path length of 25 cm. These tubes are connected with two different pressurized housings: one contains the source of a collimated light beam, the other holds the detector. Spectral measurements at 412, 440, 488, 510, 555, 630, 650, 676 and 715 nm (bandwidth of ten nm) are obtained filtering the light source. The absorption tube has a reflecting internal surface made of quartz with an air chamber inside, and a large area detector; the internal surface of the attenuation tube is non-reflective, and the light is collected through a collimated detector.

The AC-9 data processing consists of two parts. The first stage is performed with the WETLabs LABVIEW software, which corrects the dependence of the instrument response on its internal temperature, and transforms raw data to physical values. Specifically, the manufacturer protocol prescribes that absorption and attenuation of the pure water (W) correspond to the *zero* of AC-9 calibrated data. For this purpose, the LABVIEW software removes from the instrument reading the pure water calibration coefficients (*i.e.*, the instrument response determined by the manufac-

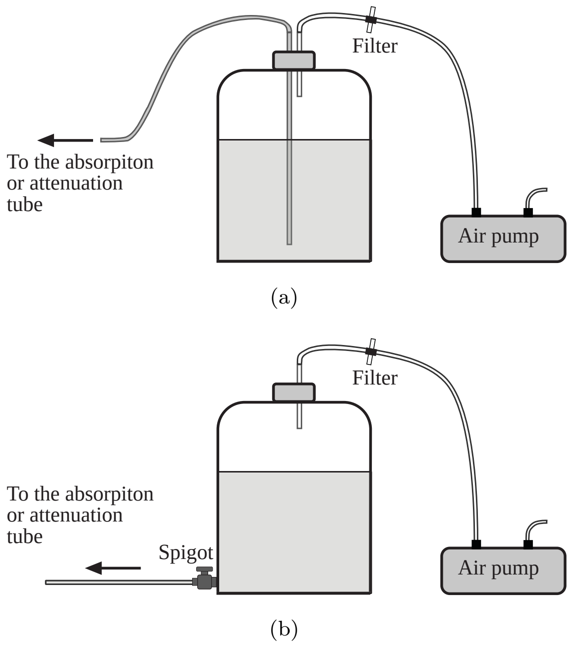


FIGURE 1: Two different configurations to get the Mili-Q water from the carboy. The configuration of panel 1(a) is recommended by the manufacturer. The configuration of panel 1(b), tested during the BIOME-04 campaign, is very effective to reduce the presence of air bubbles in the calibration water.

turer with Mili-Q water).

The second stage of the data processing includes corrections for: *i.* variations of the instrument response; *ii.* seawater *temperature-salinity* effects; and *iii. scattering* effects. These corrections, presented in the following paragraphs, are implemented with a user developed processing code.

2.1.1 AC-9 calibration

A periodic calibration of the AC-9 meter is suggested by the manufacturer because this device is sensitive to minor shocks, for instance during the shipping and deploying. Also, the user calibration ensures that the optics are clean and the instrument performs correctly. Conforming to the manufacturer recommendations, the following protocol is applied to determine the *user calibration coefficients* during the BIOME-04 campaign.

- The attenuation and the absorption tubes are disassembled. They are first washed with soap (0.1% solution). Then, they are rinsed with Mili-Q water, cleaned with isopropanol (10% solution), and once again rinsed with Mili-Q water. Finally, Kimwipes are pushed through the tubes with the aid of a plastic stick.
- The same sequence (soap - Mili-Q water - methanol - Mili-Q water) is used to clean the optics.
- The Mili-Q water (20 l) is left to degas storing the filled carboy for at least 12 hours before performing the calibration. The water is pressurized to 10 Psi connecting an air pump to the carboy cap. Particles in the air are trapped with a filter (Figure 2) to avoid water contamination.
- Calibration data are collected for few minutes, after switching on the meter and letting the water flow into the a or c tube until the flux is free from air bubbles. Data are corrected for the instrument internal temperature, and transformed into physical values applying the manufacturer calibration coefficients using the LABVIEW software. Corrections for variations of the pure water optical properties due to the difference between the user and the manufacturer water temperature* are also applied.

Table 1 and Figure 2 present the AC-9 calibrations results performed during the BIOME-04 cruise. For each assessment, the user calibration coefficients are the mean of the data collected when the instrument response is stationary, possible with a noise level (data standard deviation) less than $0.002\,\mathrm{m}^{-1}$. According to the manufacturer guidelines, user calibration coefficients with absolute values less than $0.005\,\mathrm{m}^{-1}$ indicate an adequate sensor performance. Because the instrument is noisier at the shortest wavelengths, absolute values of the order of $0.01\,\mathrm{m}^{-1}$ are still acceptable between 412 and 488 nm. Variations above these threshold indicate possible anomalies to be further assessed with an instrument revision.

The manufacturer provides *air* calibration coefficients besides those for the pure water. These values set the zero of the instrument response when data are collected in air. The instrument cleaning follows the same protocol described above for the water calibration. Air calibration is performed with the tubes and the optics completely dry. Air calibration coefficients allows monitoring the instrument without using the pure water. Section 2.3 gives an example of

*The corrections of the AC-9 data for the effects of the instrument internal temperature is a process different an independent from the correction for the variation of the water optical properties due to differences between the temperature of the water used during the calibration and the water sampled during operational measurements (see Section 2.2.2).

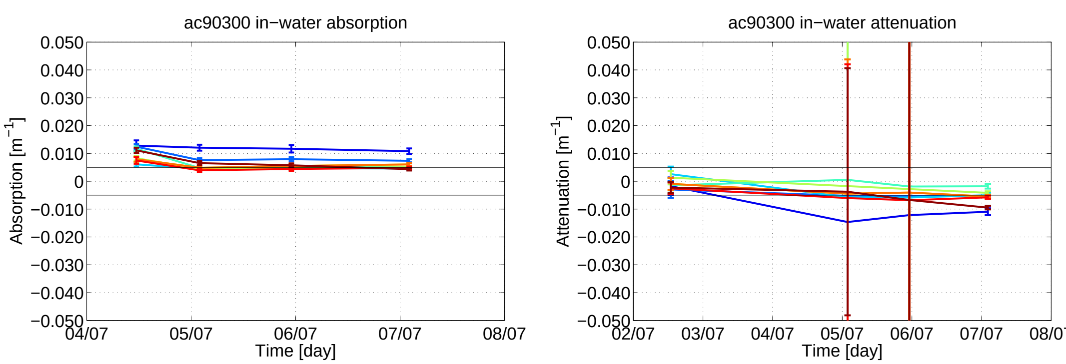
Date	Time	Temp		412	440	488	510	555	650	650	676	715
04/07/2006	11:25	21.2	μ	0.0128	0.0125	0.0061	0.0117	0.0083	0.0079	0.0079	0.0075	0.0111
			σ	0.0019	0.0009	0.0008	0.0008	0.0008	0.0009	0.0009	0.0012	0.0009
05/07/2006	01:56	21.7	μ	0.0121	0.0076	0.0045	0.0048	0.0044	0.0049	0.0049	0.0039	0.0065
			σ	0.0011	0.0007	0.0006	0.0006	0.0007	0.0006	0.0006	0.0006	0.0007
05/07/2006	23:02	21.4	μ	0.0117	0.0079	0.0047	0.0052	0.0047	0.0055	0.0055	0.0044	0.0058
			σ	0.0013	0.0007	0.0006	0.0006	0.0007	0.0006	0.0006	0.0007	0.0007
07/07/2006	02:05	21.1	μ	0.0108	0.0074	0.0046	0.0051	0.005	0.0061	0.0061	0.0048	0.0043
			σ	0.0010	0.0005	0.0005	0.0005	0.0005	0.0004	0.0004	0.0005	0.0005

(a)

Date	Time	Temp		412	440	488	510	555	650	676	715
02/07/2006	12:55	22.1	μ	-0.0018	-0.0029	0.0026	-0.0014	0.0013	-0.0009	-0.0025	-0.0022
			σ	0.0031	0.0030	0.0027	0.0026	0.0024	0.0022	0.0021	0.0019
05/07/2006	01:50	21.7	μ	-0.0146	-0.0052	-0.0058	0.0005	-0.0017	-0.0044	-0.0060	-0.0038
			σ	0.0753	0.0724	0.0660	0.0630	0.0549	0.0482	0.0481	0.0444
05/07/2006	23:07	21.4	μ	-0.0122	-0.0053	-0.0058	-0.0019	-0.0028	-0.0040	-0.0068	-0.0067
			σ	0.0912	0.0823	0.0752	0.0720	0.0666	0.0613	0.0607	0.0571
07/07/2006	02:12	21.1	μ	-0.0109	-0.0053	-0.0050	-0.0018	-0.0042	-0.0055	-0.0058	-0.0095
			σ	0.0013	0.0008	0.0009	0.0008	0.0006	0.0005	0.0006	0.0007

(b)

TABLE 1: AC-9 calibration coefficients (absorption and attenuation in panel 1(a) and 1(b), respectively). The Time is expressed as Greenwich Mean Time, and the temperature in Celsius. The calibration coefficient, μ, is the mean value of data collected for at least one minute, and σ is the corresponding standard deviation. The second and the third calibration of the attenuation meter are significantly noisy, probably due to the presence of bubbles within the tubing. These values are not used for correcting field measurements. All these calibrations are performed on board where it is difficult to reproduce ideal laboratory conditions.



(a) (b)

FIGURE 2: AC-9 a and c calibration data in panel in panel 2(a) and 2(b), respectively. Results between $\pm$ 0.005 indicate acceptable deviations with respect to the manufacturer characterization of the instrument.

outcomes obtained during the BIOME-04 cruise from air calibration data.

2.2 Correction schemes

2.2.1 Calibration correction

Designate with $\mu_x(\lambda, t_i)$ the coefficients of the i-th AC-9 user calibration (x is either a or c; t_i and λ are the time and the wavelength, respectively). Analogously, $\widetilde{x}(\lambda, t)$ is the field measurement taken at some time t, and processed with the LABVIEW software applying the manufacturer calibration coefficients. The purpose of the calibration correction is to compensate the difference between the user and the WETLabs instrument characterization:

$$x(\lambda, t) = \widetilde{x}(\lambda, t) - \mu_x(\lambda, t), \qquad (1)$$

where $\mu_x(\lambda, t)$ is the linear interpolation for the measurement time t of the user calibration coefficients defined before and after t. For an ideal and com-

λ	Ψ_T	λ	Ψ_T	λ	Ψ_T
340	0	500	0.0001	630	0.0002
350	0	505	0.0001	635	0
360	0	510	0.0002	640	-0.0001
370	0	515	0.0002	645	0
380	0	520	0.0002	650	0.0001
390	0	525	0.0002	655	0.0002
400	0	530	0.0001	660	0.0002
405	0	535	0.0001	665	0.0002
410	0	540	0.0001	670	0.0002
415	0	545	0.0001	675	0.0001
420	0	550	0.0001	680	0
425	0	555	0.0001	685	-0.0001
430	0	560	0.0001	690	-0.0002
435	0	565	0.0001	695	-0.0001
440	0	570	0.0001	700	0.0002
445	0	575	0.0002	705	0.0007
450	0	580	0.0003	710	0.0016
455	0	585	0.0005	715	0.0029
460	0	590	0.0006	720	0.0045
465	0	595	0.0008	725	0.0065
470	0	600	0.0010	730	0.0087
475	0	605	0.0011	735	0.0108
480	0	610	0.0011	740	0.0122
485	0	615	0.0010	745	0.0119
490	0	620	0.0008	750	0.0106
495	0.0001	625	0.0005		

TABLE 2: Temperature correction coefficients, add references.

pletely stable response of the instrument, all $\mu_x(\lambda, t_i)$ are zero and $x(\lambda, t) = \widetilde{x}(\lambda, t)$.

2.2.2 Temperature and salinity correction

Indicate with $\Delta T = \widetilde{T} - \widehat{T}$ the difference between the temperature of the sampling water, $\widetilde{T}$, and the temperature of calibration water, $\widehat{T}$, used by the manufacturer. Analogously, $\Delta S = \widetilde{S} - \widehat{S}$ is corresponding salinity difference (note that $\widehat{S} = 0$). The *temperature and salinity* correction removes the offset due to ΔT and ΔS from the absorption and attenuation sampling data, $\widetilde{x}$:

$$x(\lambda) = \widetilde{x}(\lambda) - [\Psi_T(\lambda) \cdot \Delta T + \Psi_{S,x}(\lambda) \cdot \Delta S]. \quad (2)$$

The correction coefficients, $\Psi_T(\lambda)$ and $\Psi_{S,x}(\lambda)$, are derived through linear interpolation of data reported in Table 2 and Table 3 (note that the temperature correction coefficients are the same for a and c)[].

2.2.3 Scattering correction

The AC-S overestimates the absorption of the water medium because the reflecting inner surface of the absorption tube does not collect all of the light scattered from the source beam. Correction schemes implemented in the user processing code are presented hereafter, and the first method is that used during the BIOME-04 campaign.

λ	$\Psi_{S,a}$	$\Psi_{S,c}$
412	0.00018	0.00007
444	0.00008	-0.00007
488	0.00008	-0.00007
510	0.00009	-0.00007
532	0.00004	-0.00008
555	0.00008	-0.00008
650	0.00011	-0.00005
676	0.00008	-0.00007
715	-0.00018	-0.00032
750	0.00070	0.00590
850	-0.00034	0
900	-0.00264	0
975	0.00221	0

TABLE 3: Salinity correction coefficients, add references.

Subtraction of the absorption at a reference wavelength The absorption by particulate and dissolved material is negligible at the highest wavelengths. Assume that: *i.* the signal detected at 715 nm is an artifact due to the scattering detection limitation; and *ii.* this offset is independent on the wavelength. The resulting correction is:

$$a(\lambda) = \widetilde{a}(\lambda) - \widetilde{a}(715), \quad (3)$$

where the tilde notation indicates measured values.

Removal of a fixed proportion of the scattering coefficient This method assumes that the missing scattering contribution to the absorption data is a fixed proportion of the scattering coefficient $b(\lambda)$, where $b(\lambda) = c(\lambda) - a(\lambda)$. The absorption correction is:

$$a(\lambda) = \widetilde{a}(\lambda) - \epsilon \cdot [\widetilde{c}(\lambda) - \widetilde{a}(\lambda)], \quad (4)$$

where the coefficient ϵ ranges between 0.14 for waters where biological particles dominate scattering, and 0.18 when sediments dominate the scattering [].

Use of a reference wavelength to determine the scattering proportion to be subtracted from the absorption This method is based on the following hypothesis: *i.* the absorption coefficient of particulate and dissolved materials is zero at some reference wavelength (*i.e.*, 715 nm); and *ii* the shape of the volume scattering function is independent of wavelength. Absorption corrected data are given by

$$a(\lambda) = \widetilde{a}(\lambda) - \frac{\widetilde{a}(715)}{[\widetilde{c}(715) - \widetilde{a}(715)]} \cdot [\widetilde{c}(\lambda) - \widetilde{a}(\lambda)]. \quad (5)$$

This correction scheme is analogous in principle to the second method, but the coefficient ϵ is here derived from absorption and attenuation values.

2.3 Attenuation and absorption (AC-S)

The AC-S is a hyper-spectral absorption and attenuation meter with 88 channels between 400 and 730 nm. It has the same water flow-through system, and employs the same 25-cm path length tubes, as the AC-9. Each sampling channel has a FWHM of 15.5 nm and the step between channels is 4 nm.

The AC-S cleaning, calibration and data processing is the same as for the AC-9 meter. AC-S user calibration coefficients collected during the BIOME-04 cruise are in Table 4 and Figure 3. Because the attenuation calibration coefficients are outside the range of tolerance indicated by the manufacturer, the AC-S device was sent for a revision after the BIOME-04 campaign.

Figure 4 shows an unexpected data *quantization* effect. This effect, noticed during the BIOME-04 cruise, is mostly occurring in the blue region of the spectra of attenuation and absorption values.

2.4 Back-scattering (ECO BB-9)

Seawater back-scattering at 412, 440, 488, 510, 532, 595, 660 and 676 nm is measured with an ECO BB-9 meter (ECO stands for Environmental Characterization Optics) manufactured by WETLabs. This device is made by three independent meters (BB-3) hosted in the same pressure housing. Each sub-unit measures the back-scattering at three different wavelengths. As shown in Figure 5, backscattering measurements are taken at 117° degrees with respect to the direction of the incident light because this minimizes the error in extrapolating to the total backscattering coefficient [Boss and Pegau, 2001].

2.4.1 Correction for seawater absorption

Light scattered from the sampling volume travels across the seawater before reaching the detector. This means that the measured signal has to be corrected for the attenuation and the absorption of the water medium. The manufacturer calibration compensates for the attenuation contribution. Instead, the absorption contribution to the volume scattering measured at 117°, $\widetilde{\beta}(117°, \lambda)$, has to be rectified on the basis of coincident absorption measurements, $a(\lambda)$:

$$\beta(117°, \lambda) = \widetilde{\beta}(117°, \lambda) \exp(0.039 \cdot a(\lambda)). \quad (6)$$

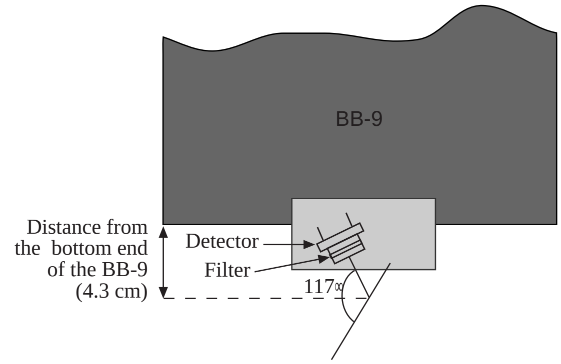


FIGURE 5: Measurement angle and sampling point of the ECO BB-9 meter.

The corrected value represents the joint volume scattering at 117° of suspended particles and pure water.

The data processing software provided by WETLabs (see Section 2.9.3) applies the manufacturer calibration coefficients to transform raw ECO BB-9 readings into calibrated physical (the calibration of the ECO BB-9 can not be performed by the user).

2.4.2 Data products

The manufacturer software provides the following data products: 1) Volume scattering of particles at 117°; 2) Backscattering of particles; and 3) Total backscattering. The processing scheme to derive these data products is described hereafter. The manufacturer processing code does not implement the correction of Equation 6. Because all data products depend on this correction, ECO BB-9 measurements taken during the BIOME-04 cruise are recomputed with a user processing code after applying absorption adjustment.

Volume Scattering of Particles at 117° The particle volume scattering, $\beta_p(117°, \lambda)$, is computed removing the pure water contribution, $\beta_W(117°, \lambda)$, from the volume scattering:

$$\beta_p(117°, \lambda) = \beta(117°, \lambda) - \beta_W(117°, \lambda); \quad (7)$$

where $\beta_W(\theta, \lambda)$ is given by

$$\begin{aligned} \beta_W(\theta, \lambda) \quad = \quad & 1.38(\lambda/500\,\text{nm})^{-4.32}(1 + 0.3 \cdot S/37) \cdot \\ & 10^{-4}(1 + \cos^2\theta(1 - \delta/(1 + \delta))), \end{aligned}$$

with $\delta = 0.09$, and S the salinity [Morel, 1974].

Backscattering of Particles The particulate backscattering, b_{bp} is derived from the volume scattering

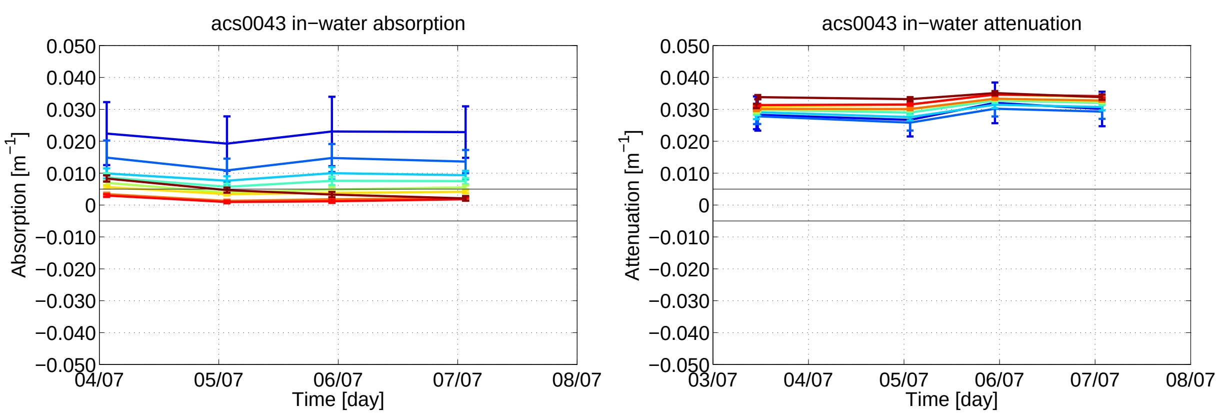
Date	Time	Temp		411.7	438.4	487.8	508.7	556.5	629.2	649.4	677.5	713.7
04/07/2006	01:29	21.7	μ	0.0224	0.0149	0.0099	0.0087	0.0070	0.0056	0.0034	0.0030	0.0083
			σ	0.0099	0.0054	0.0016	0.0013	0.0007	0.0004	0.0005	0.0004	0.0010
05/07/2006	01:39	21.7	μ	0.0193	0.0109	0.0076	0.0057	0.0039	0.0034	0.0013	0.0010	0.0047
			σ	0.0085	0.0037	0.0014	0.0010	0.0006	0.0004	0.0004	0.0004	0.0008
05/07/2006	22:44	21.4	μ	0.0231	0.0148	0.0100	0.0076	0.0048	0.0038	0.0018	0.0012	0.0033
			σ	0.0109	0.0044	0.0019	0.0013	0.0008	0.0005	0.0005	0.0005	0.0008
07/07/2006	01:36	21.1	μ	0.0229	0.0136	0.0094	0.0075	0.0055	0.0042	0.0021	0.0018	0.0021
			σ	0.0081	0.0036	0.0013	0.0010	0.0006	0.0004	0.0004	0.0004	0.0007

(a)

Date	Time	Temp		410.9	441.2	487.1	512.1	555.8	629.5	649.9	674.2	714
03/07/2006	10:56	22.3	μ	0.0289	0.0277	0.0281	0.0290	0.0293	0.0308	0.0298	0.0311	0.0311
			σ	0.0051	0.0024	0.0012	0.0007	0.0005	0.0003	0.0003	0.0004	0.0007
03/07/2006	11:17	22.3	μ	0.0283	0.0278	0.0291	0.0299	0.0298	0.0308	0.0302	0.0314	0.0338
			σ	0.0050	0.0024	0.0010	0.0008	0.0005	0.0003	0.0003	0.0004	0.0007
05/07/2006	01:32	21.7	μ	0.0267	0.0258	0.0276	0.0290	0.0299	0.0315	0.0301	0.0315	0.0332
			σ	0.0052	0.0025	0.0010	0.0008	0.0005	0.0003	0.0004	0.0004	0.0006
05/07/2006	22:50	21.4	μ	0.0320	0.0302	0.0315	0.0328	0.0332	0.0346	0.0333	0.0346	0.0351
			σ	0.0064	0.0024	0.0011	0.0008	0.0005	0.0004	0.0003	0.0004	0.0006
07/07/2006	01:45	21.1	μ	0.0301	0.0293	0.0307	0.0320	0.0324	0.0338	0.0328	0.0341	0.0338
			σ	0.0054	0.0023	0.0010	0.0008	0.0005	0.0003	0.0004	0.0004	0.0008

(b)

TABLE 4: As in Table 1, but for the AC-S data (absorption and attenuation calibration coefficients in panel 4(a) and 4(b), respectively).



(a) (b)

FIGURE 3: As in Figure 2, but for the AC-S data.

measured at 117° through

$$b_{bp}(\lambda) = 2\pi X \beta_p(117^\circ, \lambda), \tag{8}$$

where $X = 1.1$ [Boss and Pegau, 2001].

Total Backscattering To obtain the total backscattering, b_b, the pure water contribution, $b_{bW}(\lambda)$, is added to the particulate back scattering:

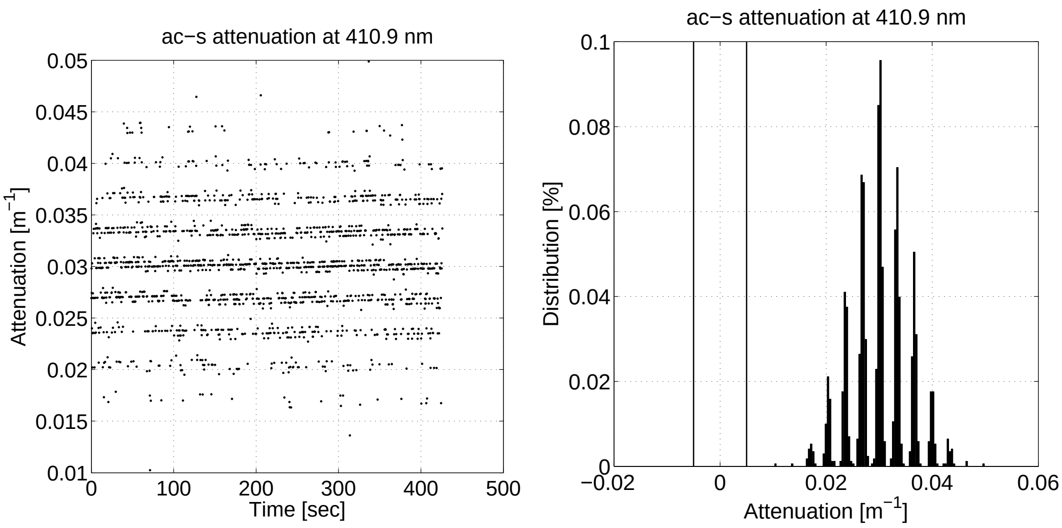
$$b_b(\lambda) = b_{bp}(\lambda) + b_{bW}(\lambda). \tag{9}$$

The value of $b_{bW}(\lambda)$ is:

$$b_{bW}(\lambda) = 0.0022533(\lambda/500\,\text{nm})^{-4.23}. \tag{10}$$

2.5 Chlorophyll concentration (*Chl-a* WETStar fluorometer)

The WETStar fluorometer, manufactured by WET-Labs, measures the *Chl-a* concentration on the basis of fluorescence emission properties. The water sample is flushed through a quartz tube within the WETStar meter. Here, it is excited by two bright blue LED



(a) (b)

FIGURE 4: Time series of attenuation data taken in-air with the AC-S meter and corresponding data distribution in Panel 4(a) and 4(b), respectively. The data quantization effect, and the concomitant sub-quantization with a drift in time, were noticed during the BIOME-04 cruise.

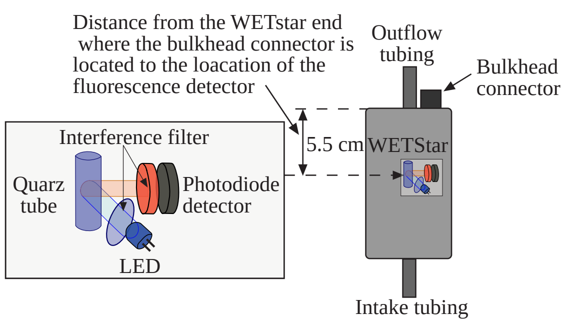


FIGURE 6: *Chl-a* fluorescence measurement scheme and sampling point location of the WETStar meter.

light sources (centered at 470 nm and modulated at 1 kHz). The sampling volume, approximately 0.25 cm^3, is defined by the intersection of the excitation light with the field of view of the detector, within the quartz flow tube (see Figure 6). The fluorescence signal, filtered to remove any scattering contribution from the emission light, is measured at 695 nm by a detector positioned at 90 degrees with respect to the direction of the LEDs emission and the quartz tube axis. The instrument has an analog output between 0-5 VDC, which corresponds to a 0.03–75 μg l^{-1} dynamic range. The nominal sampling frequency of *Chl-a*-WETStar is 6 Hz.

2.6 Colored Dissolved Organic Matter (CDOM WETStar Fluorometer)

The CDOM WETStar is also manufactured by WET-Labs and is based on the same technology of the *Chl-a* WETStar. The excitation and emission channels are at 370 nm (10 nm FWHM) and 460 nm (120 nm FWHM (verify...)), respectively. The CDOM Fluorometer is calibrated by the manufacturer with a solution of Quinine Sulfate Dehydrate (QSD) at a concentration of 100 parts per billion (ppb). The corresponding dynamic range of the instrument is 0–350 ppb. The nominal sampling frequency of CDOM WETStar is 6 Hz.

Because QSD was used for the sensor calibration, and due to the variability of the CDOM fluorescence property in natural environments, the CDOM WET-Star can only provide a rough estimate of the CDOM concentration.

2.7 Photosynthetically Available Radiation

The Photosynthetically Active Radiation between 400 and 700 nm is measured with a QCP-2000 Cosine PAR sensors manufactured by Biospherical Instruments Inc. 5340 Riley Street, San Diego, CA 92110 USA. This single channel detector utilizes a silicon photo detector with a flat quantum response over PAR. The sampling frequency is 1 Hz. Spectral response-induced errors cause less than 5% error in

	Temp. [o C]	Cond. [S/m]	Press. [m]
Meas. Range	-5 to $+35$	0 to 9	0 to 350
Initial Accuracy	0.002	0.0003	0.1% of full scale range
Typical Stability	0.0002	0.0003	0.004% of full scale range
Resolution	0.0001	0.00005	0.002%

TABLE 5: Measurement specifications of the SBE 49 FastCAT CTD device.

naturally occurring light fields. The sensor is calibrated in quanta cm^{-2} sec^{-1}†. Nominal sensitivity is 1 volt = 1×10^{17} quanta cm^{-2} sec^{-1} (slightly less than full sunlight). Noise level is typically less than 1 millivolt. The measurement PAR dynamic range is 1.4×10^{-5}– 0.5 μE cm^{-2} sec^{-1}.

2.8 Temperature and salinity (CTD)

Seawater salinity and temperature is measured with a SBE 49 FastCAT device manufactured by Sea-Bird Electronics, Inc. 1808 136th Place NE Bellevue, Washington 98005 USA. The CTD device holds the pressure sensor, and the sampling depth of the data collected with the other devices is derived from the CTD pressure sensor through a linear interpolation of the measurement time stamp. CTD sensor specifications are given Table 5.

2.9 Data acquisition

The data acquisition is controlled through a personal computer (PC). The communication between the PC and the measurement devices deployed with the IOP-frame (which is presented in Section 3) is set through the scheme of Figure 7.

2.9.1 Data communication and storage

The PC is connected to the DEC unit with a serial cable. The DEC unit, which also transforms the input 110 volt AC into 48 volt DC, is further connected with the *sea cable* to the *submersible unit* mounted on the IOP-frame. The submersible unit transforms the 48 volt DC into 12 volt DC. The ensemble of the DEC unit and the submersible unit is called Communication and Conversion System, PCCS.

The submersible unit is attached to the Data Handler system, DH-4. All the measurement devices are

†The conversion between Quanta and μE (micro-Einstein) is: 6×10^{13} quanta cm^{-2} sec^{-1} =1 μE cm^{-2} sec^{-1}.

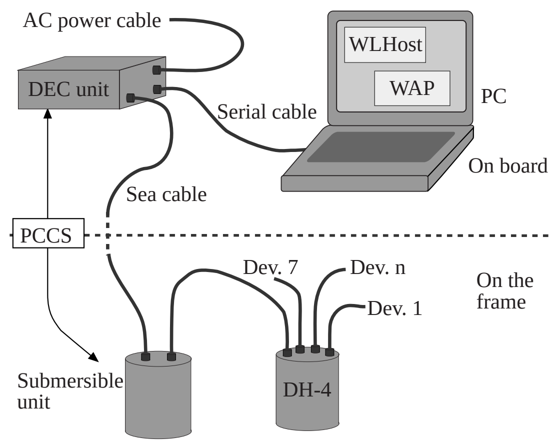


FIGURE 7: Data communication scheme. The PCCS is made by two components: the DEC unit (one board); and the submersible unit (on the IOP-frame). The DEC is connected to the personal computer, while the submersible unit attached to the DH-4. All measurement devices are plugged into the DH-4. As an example, only three connections are shown here.

then plugged into the DH-4. The DH-4 is a processing unit for power supply, time stamping and data storage.

The PCCS and the Host software are manufactured by Manufactured by Wet Labs, 620 Applegate St. Philomath, OR 97370, USA.

2.9.2 The Host software

The DH-4 operations are controlled through the WETLabs WLHost software installed on the PC located on board. The WLHost software sets the DH-4 communication ports and corresponding protocols. Table 6 details for each measurement device, and for the PCCS system, the set of configurations used for the BIOME-04 campaign. Note that the nominal sampling frequency of the data handler system is 6 Hz. This is a manufacturer constraint. Although the CTD sampling frequency is 8 Hz, nonetheless time stamps are given with a maximum frequency of 6 Hz. And as a consequence, different CTD reading are recorded with the same time stamp.

The WLHost software also sets the DH-4 data storage mode. Specifically, the data stream from the instrument devices can be optionally: *i.* stored in an *archive file* in the DH-4 internal flash memory; *ii.* sent in real time to the PC; or *iii.* both stored and sent at the same time. The WLHost software does not permit to save real time data on the PC during mea-

Device ID	Device configuration					DH-4 connection
	Meter	SN	Data type	Bound Rate	Data Rate	
0	PCCS	088	BINARY+ASCII	115200	6 Hz	1
1	AC-S	43	BINARY	115200	4 Hz	2
2	AC-9	156	BINARY	19200	6 Hz	3
3	SBE49 CTD	4942127-0076	ASCII	9600	8 Hz	4
4	BB-9	274	ASCII	19200	1 Hz	5
5	Flow sensor	28	ASCII	9600	1 Hz	7
6	PAR	QCP-2150	ASCII	9600	1 Hz	8
7	CDOM	297P	ANALOG		6 Hz	10
	Chl-a	1096	ANALOG		6 Hz	

TABLE 6: Meter, PCCS and DH-4 settings for the BIOME-04 campaign. The device ID number (first column) refers to the schematic representation of Figure 7.

surement operations. Data are transmitted only for basic visualization and quality check purposes. The archive file is uploaded from the DH-4 flash memory to the PC hard drive with the WLHost software at the end of the cast.

Only data in a text format can be visualized in real time with the WLHost software selecting one instrument at the time. Furthermore, the WLHost software only handles raw instrument readings and not calibrated physical values. An indirect visualization can be performed with WLHost software re-sending the data stream of one (or more) device(s) to the available serial port(s). Measurements have then to be diverted as output to different serial ports using cables with the input and the output pin inverted. Afterwards, data can be read, calibrated and visualized, for instance using the instrument software provided by the manufacturer. This scheme virtually gives a real time access to calibrated data from all instruments. In practice, it is not effective because it requires many serial ports available, serial cables with input and output pin inverted, and many different softwares running at the same time.

2.9.3 The WAP software

The purpose of WETLabs Archive File Processing (WAP) software is to extract the values measured by the different sensors from the archive file loaded on the logger PC, and applies the calibration coefficients. It also optionally allows to merge into an unique ASCII file data taken from different sensors. No plotting functionalities are provided with the WAP software. The only effective IOP data visualization and quality check experienced during the BIOME-04 cruise is with the user processing code. Because of the time to upload the archive file with the WLHost software, and to extract and calibrate the data with the WAP software, possible measurement problems can be detected when the IOP-frame is on board. That is too late to repeat the cast due to the other activities scheduled in the campaign.

3 IOP-frame

3.1 Frame structure

The IOP-frame is a structure assembled with aluminum components (Figure 8). Horizontal bars located between the uprights of the external skeleton hold the measurement devices. These bars can be removed and repositioned to reconfigure the frame and / or add new instruments.

3.2 Tubing scheme

The tubing for the seawater sampling starts from a single inlet to ensure the specimen homogeneity (Figure 10). Four pipelines connect the inlet to the intakes of the attenuation and absorption tubes of the AC-9 and AC-S meters. The connection to the absorption tube of the AC-9 device has a set of valves for selecting a *direct path*, or a *filtering path*. In the latter case, two filters (5.0 μm and 0.2 μm pore size) sequentially capture the particulate material suspended in the seawater.

From the AC-9 absorption tube, the water goes into the CDOM fluorometer. According to the path selection, CDOM measurements can optionally be taken with filtered or un-filtered water. The tubes from the CDOM fluorometer and from the outtake of the AC-9 attenuation meter are then jointed before going into the outlet.

A different tubing scheme is set for the AC-S and the *Chl-a* fluorometer. Because here there is no a *filtering path*, all the water from two AC-S tubes goes going into the *Chl-a* fluorometer.

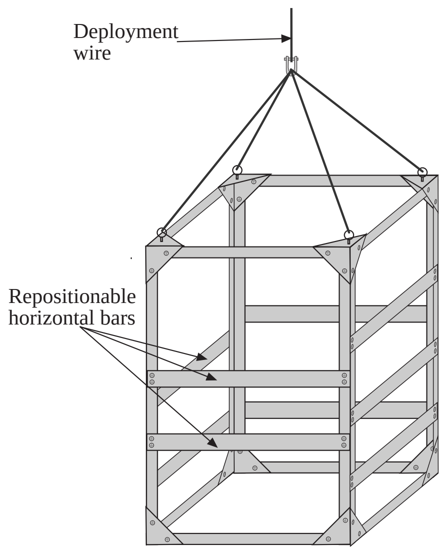


FIGURE 8: Structure of the IOP-frame with the horizontal bars holding the instruments.

Debubblers are positioned after the AC-9 and AC-S in the highest point of the tubing. The water flow is regulated with two valves and monitored with two flow sensors in order to have about the same overall rate through the AC-9 and AC-S tubes. Finally, two pumps manufactured by Sea-Bird (one powered with the AC-9 and one with the AC-S) jointly pull the water out of the outlet.

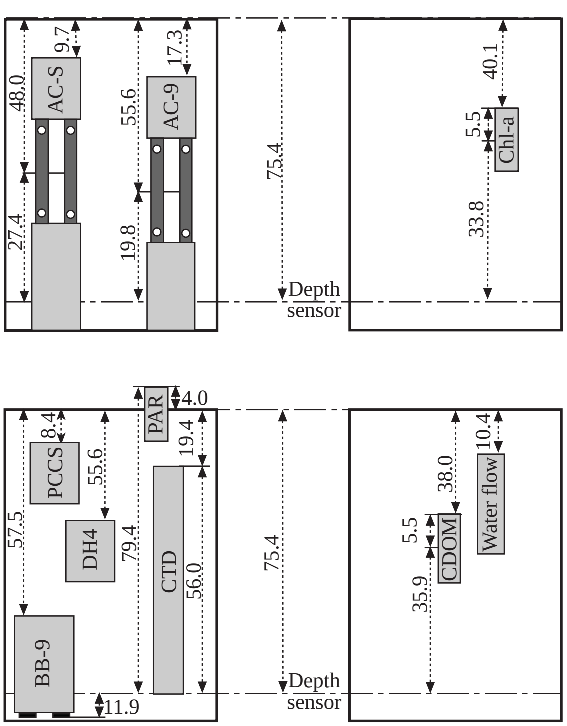


FIGURE 9: Device positions and measurement point offsets with respect to the location of the pressure sensor situated at the bottom of the CTD meter. Each panel of this figure corresponds to a different side of the IOP-frame (Figure 8).

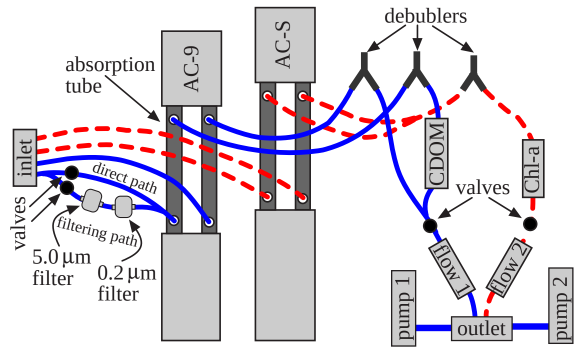


FIGURE 10: The IOP-frame tubing scheme.

3.3 Deployment protocol

The IOP-frame was deployed from the back frame of the ship. In order to purge the air from the tubing, pumps are run for at least 3 minutes with the IOP-frame was at 10 m depth (or two meters above the bottom if the sea bottom if the depth of the water column was less than 10 meters). After checking that the water flow is stationary and of about 2l/min, the IOP-frame is deployed to two meters from the sea

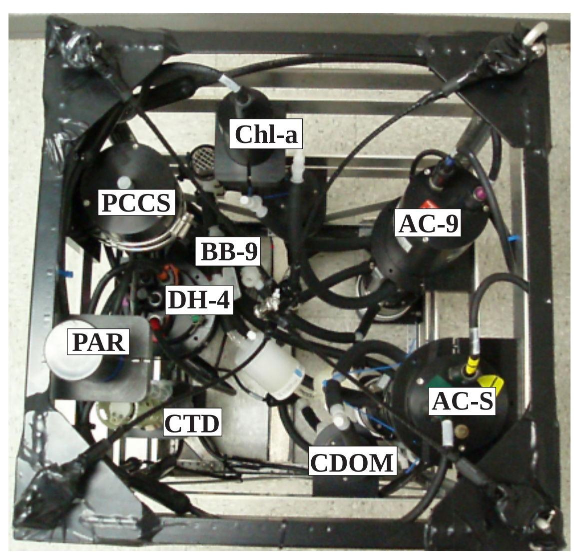


FIGURE 11: View from above of the devices mounted on the IOP-frame.

Station Num.	Cast Num.	GMT Date	GMT Time	Lat.	Lon.	AC-S a	AC-S c	AC-9 a	AC-9 c	WStar CDOM	WStar *Chl-a*	BB-9 b_b
1b4	1	02/07/06	14:32	37.702	-75.296	0	0	0	2	1	0	3
2b4	2	02/07/06	17:07	37.638	-75.147	0	0	0	1	0	0	1
3b4	3	02/07/06	18:55	37.528	-75.039	0	0	0	0	0	0	1
4b4	4	02/07/06	21:15	37.387	-74.939	0	0	0	0	1	1	1
4b4	5	02/07/06	21:31	37.389	-74.936	0	0	0	0	0	0	1
9b4	6	03/07/06	16:57	36.604	-75.053	0	0	0	1	0	1	1
10b4	7	03/07/06	19:39	36.536	-75.270	0	0	0	2	0	0	1
11b4	8	03/07/06	21:13	36.507	-75.385	0	2	0	2	0	0	1
15b4	9	04/07/06	13:32	36.800	-75.854	0	1	0	3	3	0	1
16b4	10	04/07/06	15:15	36.670	-75.770	0	0	0	2	0	0	1
17b4	11	04/07/06	17:51	36.887	-75.722	0	0	0	1	3	0	1
18b4	12	04/07/06	19:53	36.916	-75.555	0	2	1	2	0	0	1
19b4	13	04/07/06	21:59	37.097	-75.702	0	0	0	1	0	1	1
19b4	14	04/07/06	22:06	37.098	-75.702	0	0	0	1	0	0	1
25b4	15	06/07/06	10:40	38.542	-74.495	0	0	3	1	3	0	1
26b4	16	06/07/06	12:42	38.586	-74.676	0	0	0	1	0	0	1
26b4	17	06/07/06	12:49	38.584	-74.677	0	0	1	0	0	0	1
27b4	18	06/07/06	14:20	38.659	-74.808	0	0	0	2	3	0	1
28b4	19	06/07/06	16:40	38.640	-74.984	0	0	0	0	3	0	0
29b4	20	06/07/06	18:12	38.776	-74.985	0	0	0	3	3	0	0
30b4	21	06/07/06	19:30	38.890	-75.057	0	0	0	1	3	0	0
31b4	22	06/07/06	20:53	38.913	-75.115	0	0	0	3	3	0	1

Table 7: Deployment stations and Quality Control (QC, see text) flags for the IOP data collected during the Biome-04 cruise.

bottom and the data collection starts.

The IOP-frame is lift up to sea surface with an average speed of 20 cm/s. Only up-cast measurements are taken to reduce the side effects of residual air bubbles. After the cast, the IOP-frame is brought onto the deck of the ship, rinsed and covered with a white fabric to avoid overheating.

The deployment depth is given by the CTD pressure sensor, and the offset of the measurement point of each device mounted on the IOP-frame with respect to this sampling depth is shown in Figure 9.

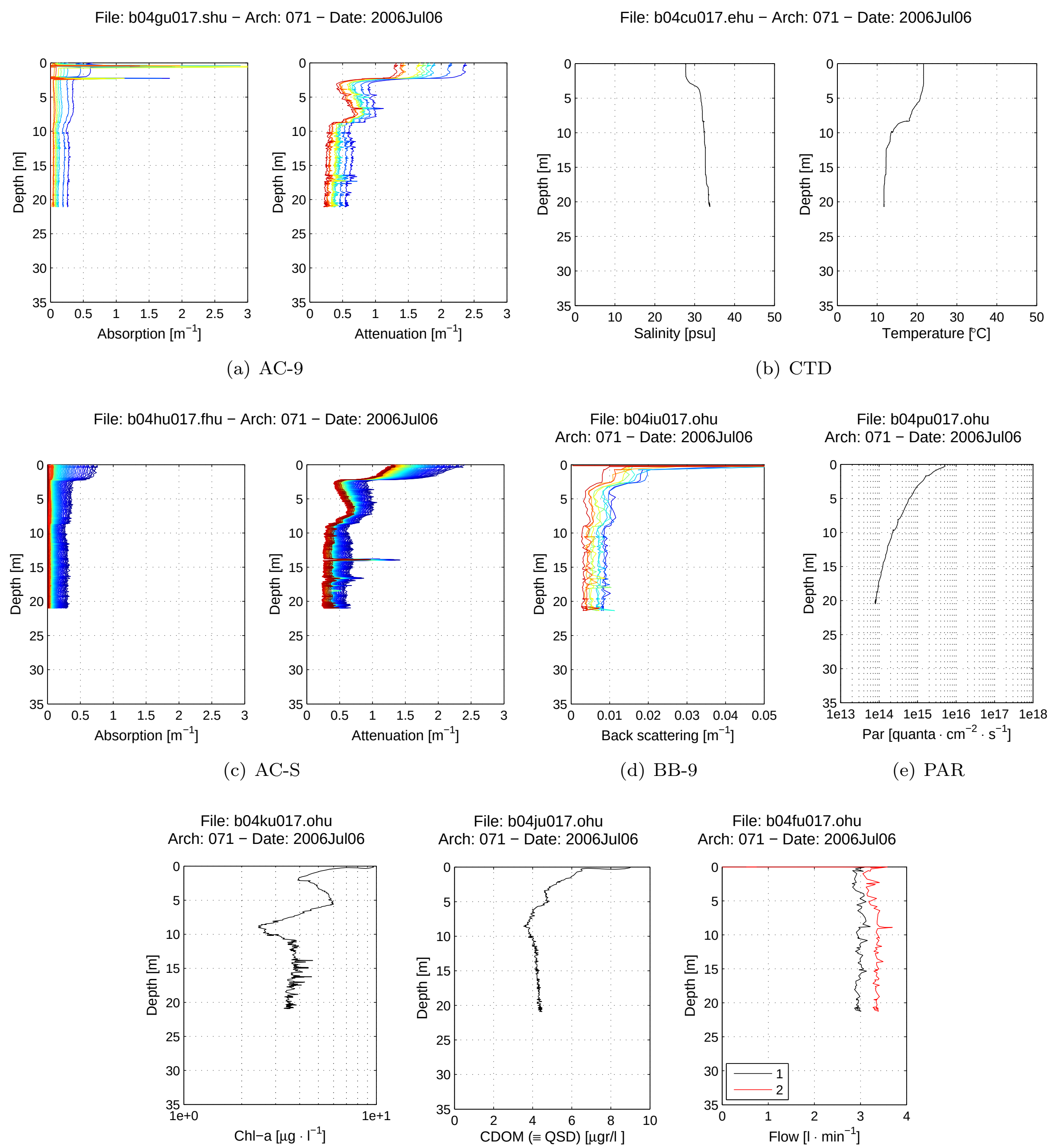
4 Field measurements

The list of IOP-frame deployments performed during the Biome-04 cruise is reported in Table 7. Data of Figure 12 show, as an example, the full set of measurement profiles taken with the IOP-frame during the cast number 17. Measurements from this cast are further discussed in Section 4.3 in a case study comparison between AC-9 and AC-S data.

4.1 Quality Control

Each measurement profile is classified with a Quality Control (QC) value defined as follows. QC values range between 0 and 3, with 0 indicating the highest quality data for cal / val processing. QC = 1 flags samples with minor problems that can be used without any correction for data analysis and algorithm development. QC = 2 refers to data that can not be used as they are, but require correction (e.g., spike removal). Data that are not reliable and can not be used even if corrected are flagged with QC = 3. QC values are in Table 7.

These results show that: *i*. The ECO BB-9 data starts out usually noisy, getting better as the cruise progresses; the only nominal data (very little noise) occur at the end of the cruise in the most turbid water. *i*i. Data taken with the AC-S are in most of the cases better than AC-9 measurements. This result is inconsistent with the IOP-frame tubing scheme because all of the water comes from one inlet, and there is nothing in the tubing configuration that would preferentially cause the degradation of one instrument with respect to the other. *i*ii. The AC-S absorption data are always nominal. *i*v.The AC-9 absorption values are almost always nominal, and usually better than the AC-9 attenuation measurements. *v*. The AC-9 data attenuation are occasionally bad. *v*i. Data taken with the *Chl-a* fluorometer are usually nominal. *v*ii. The CDOM estimates go from good to bad as the cruise progresses.



(a) AC-9 (b) CTD

(c) AC-S (d) BB-9 (e) PAR

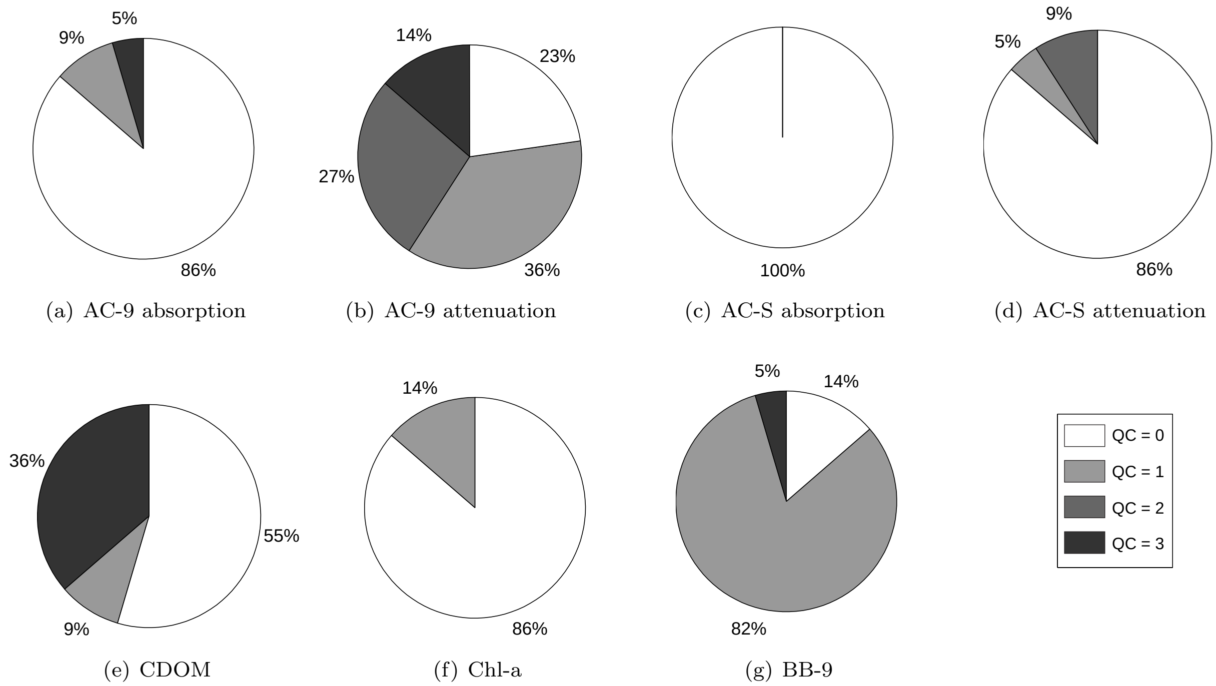
(f) *Chl-a* (g) CDOM (h) Water flow

FIGURE 12: Profile data collected during the station number 17 of the BIOME-04 campaign.

4.2 Data variability

The variability of the field measurements collected during the BIOME-04 cruise is presented in terms of percentiles, from 10% to 90% with a step of 10%. The distribution of each measured quantity is derived from measurement profiles with a QC less or equal to 0, and without accounting for the sampling depth.

Table 8 shows the data statistics for temperature, salinity, *Chl-a* and CDOM data. As an example, the CDOM value for a percentile equal to 30% is $2.9\,\mu\mathrm{gr\,l}^{-1}$ (QSD equivalent), meaning that CDOM concentration observed during the BIOME-04 cruise are 30% of the times less than $2.9\,\mu\mathrm{gr\,l}^{-1}$ (QSD equivalent).



(a) AC-9 absorption (b) AC-9 attenuation (c) AC-S absorption (d) AC-S attenuation

(e) CDOM (f) Chl-a (g) BB-9

FIGURE 13: Quality Control summary of the profile data collected during the BIOME-04 cruise.

Percentile	Temp. [C°]	Salinity [PSU]	*Chl-a* [μgr l^{-1}]	CDOM [μgr l^{-1}]
10%	12.4	28.9	2.4	1.3
20%	13.2	31.1	2.7	2.2
30%	13.6	31.6	3.0	2.9
40%	14.2	32.2	3.2	3.6
50%	15.9	32.5	3.7	4.2
60%	18.4	32.7	4.2	5.4
70%	19.7	33.1	4.5	6.3
80%	22.1	33.6	5.0	7.6
90%	23.3	34.0	6.4	10.6

TABLE 8: Percentile values for temperature, salinity, *Chl-a* and CDOM measurements. Results are based on measurement profiles with QC less or equal to 1.

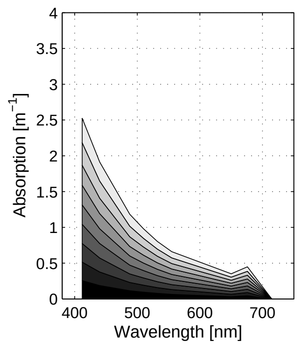
The distribution of spectral measurements (AC-9, AC-S and ECO BB-9) is summarized by means of the area plots of Figure 14. Percentiles, between 10% and 90% with step of 10%, are designed with different color.

4.3 AC-9 versus AC-S data

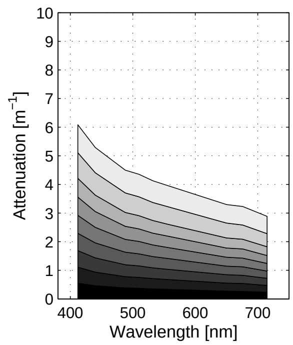
Data collected during the BIOME-04 cruise are exploited in this case study to investigate the agreement between AC-9 and AC-S data. This comparison is based on the data from the cast 17 (see Figure 12 for the entire set of measurement profiles). The tubing selection from the inlet to the AC-9 is the *direct path* and this allows to directly compare both absorption and attenuation values.

In order to compare AC-9 and AC-S data, the following 3 step procedure is adopted to remove spikes from the profile measurements:

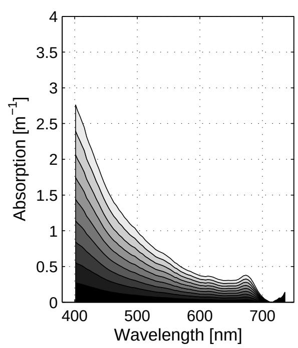
1) Profile data are smoothed applying a *moving average* algorithm with a box width set to 7. That means that the value of each measurement point is replaced with the average of the ensemble of the point itself, the 3 preceding points and the 3 following points. Smoothing results are shown in Figure 15(a) and 15(b) for attenuation and absorption data at 440 nm, respectively.
2) A comparison with profile measurements of Figure 12(a) and 12(c) shows that spikes are only reduced in the smoothed data but they do not disappear completely. Hence, the second step of the profile cleaning process is the spike localization. For this purpose, define: *i.* the *difference array* as the absolute difference between the original profile measurements and the smoothed data; and *ii.* the *tolerance level* as three times the standard deviation of the difference array. Spikes are defined as those sampling points where the difference array is above the tolerance level.
3) Once the spikes have been identified and removed, the *moving average* algorithm is once



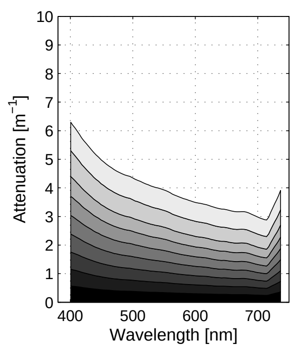
(a) AC-9 (Absorption)



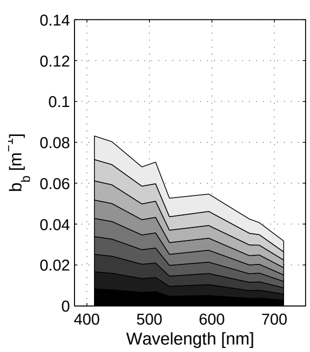
(b) AC-9 (Attenuation)



(c) AC-S (Absorption)



(d) AC-S (Attenuation)



(e) ECO BB-9 (b_b)

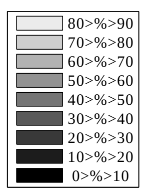
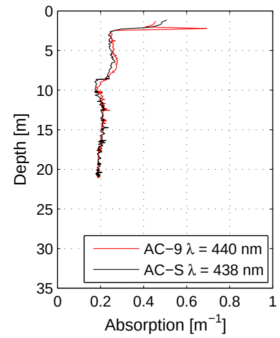
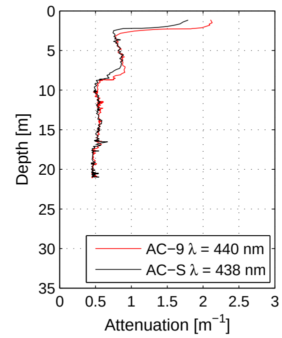


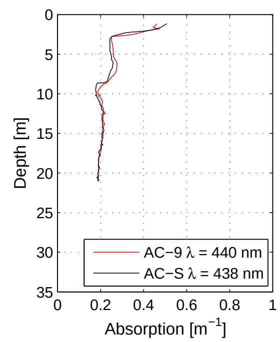
FIGURE 14: Spectral data distribution expressed in terms of percentiles.



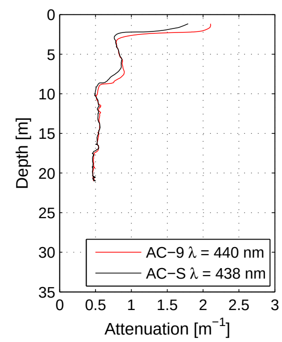
(a) Smoothed a values



(b) Smoothed c values



(c) Cleaned a values



(d) Cleaned c values

FIGURE 15: Example of the smoothed (panels 15(a) and 15(b)) and and cleaned (panels 15(c) and 15(d)) from the AC-9 and AC-S measurement taken approximately at 440 nm.

AC-9	412	440	488	510	532	555	650	676
AC-s	412	438	488	509	533	557	649	678
ρ^2	0.95	0.94	0.94	0.93	0.92	0.91	0.67	0.63

(a) Absorption

AC-9	412	440	488	510	532	555	650	676	715
AC-S	411	441	487	512	533	556	650	674	714
ρ^2	0.90	0.89	0.89	0.91	0.91	0.90	0.89	0.89	0.89

(b) Attenuation

TABLE 9: Coefficient of determination between AC-9 and AC-S data.

more applied to the original measurement profile. The comparison between AC-9 and AC-S data is based on these final *cleaned data*, which are shown in Figure 15(c) and 15(d).

This three step procedure is preferred to a simple application of the box averaging algorithm suggested by the manufacturer because the latter only spreads the spikes without really canceling their contribution.

The comparison between AC-9 and AC-S data is presented through the determination coefficients, ρ^2, of Table 9(a) and 9(b) for absorption and attenuation data, respectively. The reason to rely on ρ^2 for this comparison is because it can be interpreted as the amount of variance of the values measured with one sensor that can be explained with the amount of variance of the values measured with the other sensor. Results are derived interpolating AC-S data to the AC-9 sampling depth and excluding measurement taken at less than 1 m depth to exclude data possibly contaminated by problems that may occur close to the surface (for instance, debubblers coming out of

	412	440	488	510	532	555	650	676
412		0.985	0.955	0.948	0.884	0.851	0.418	0.294
440	0.999		0.985	0.982	0.903	0.894	0.477	0.297
488	0.995	0.998		0.991	0.947	0.936	0.569	0.386
510	0.991	0.995	0.998		0.940	0.948	0.551	0.350
532	0.988	0.992	0.997	0.999		0.972	0.668	0.567
555	0.984	0.989	0.995	0.998	1.000		0.669	0.482
650	0.969	0.977	0.987	0.991	0.995	0.997		0.636
676	0.967	0.975	0.985	0.989	0.993	0.996	1.000	
715	0.962	0.970	0.982	0.986	0.991	0.994	0.999	1.000

(a) AC-9

	412	440	488	510	532	555	650	676
412		0.982	0.937	0.931	0.898	0.842	0.688	0.758
440	0.999		0.982	0.979	0.953	0.906	0.766	0.834
488	0.993	0.997		0.996	0.977	0.943	0.838	0.890
510	0.989	0.994	0.999		0.989	0.960	0.850	0.905
532	0.984	0.989	0.997	0.999		0.988	0.864	0.915
555	0.978	0.985	0.995	0.998	0.999		0.854	0.898
650	0.952	0.962	0.978	0.985	0.990	0.993		0.978
676	0.951	0.960	0.977	0.984	0.989	0.993	1.000	
715	0.943	0.953	0.971	0.979	0.985	0.989	0.999	0.999

(b) AC-S

TABLE 10: Coefficient of determination between AC-9 (Table 10(a)) and AC-S (Table 10(b)) data. Entries above and below the diagonal refer to the absorption and attenuation data, respectively.

the water).

The determination coefficient between absorption data displays a stronger variability (0.95–0.63) than between attenuation data (0.90–0.89). Additionally, up to 555 nm the agreement between absorption values is higher than between attenuation values.

In order to have a criterion to evaluate the results, the determination coefficients between different channels of the same sensor are presented in Table 10(a) and 10(b) for AC-9 and AC-S data, respectively. In each table, the entries above the diagonal refers to absorption data, those below the diagonal to the attenuation data. Values on the diagonal are not reported because they are all equal to one.

Results shows that: *i.* for both AC-9 and AC-S data, the agreement between attenuation values at different channel is higher than between absorption values; *ii.* the c variability is lower between different channels of the same instrument than between the same channel of different instruments; and *iii* the agreement at different channels is of the same order for the AC-9 and AC-S data in the first sampling wavelengths, but this correspondence reduces for the absorption data measured at 650 and 676 nm with the AC-9 meter.

These outcomes are consistent with what observed comparing values taken at the same channels with the two instruments. Specifically, it can be noticed that the most noisy data are the absorption values taken with the AC-9 above 555 nm. The signal to noise ratio is highest at these wavelengths, and this can in part explain why the absorption values measured with the AC-9 at the highest wavelengths are the most noisy.

Further investigations, out of the scope of this report, are going to be undertaken to explain: *i.* the difference between ρ^2 of the AC-9 and AC-S absorption data presented in Table 10; and *ii.* why up to 550 nm, ρ^2 between absorption data is higher than the ρ^2 between attenuation data.

5 Summary and Conclusions

During the BIOME-04 cruise, IOP data were taken with a set of instruments mounted on the IOP-frame. Although this was the first field campaign, the IOP-frame proved to be an effective and easily reconfigurable structure to be used in the field activities.

An adjustable tubing configuration was set to optionally select a *direct* or a *filtered path* from the inlet to the AC-9 absorption tube. This seawater filtering was applied by different investigators (add references!) using resources analogous to those exploited by the Authors of this report. Still data collected during the BIOME-04 cruise showed the limits of this scheme. Specifically, it was found that the water flow rate can not be kept at acceptable levels due to the excessive clogging effect of the 5.0 μm and 0.2 μm pore size filters. The use different strategies to increase the flow rate through the filters is now under investigation.

Data were collected and processed with the WETLabs software. This system proved to be capable of handling the complexity (different formats and sampling rates) of the data streams from the instruments set. Still, the experience gathered during the BIOME-04 cruise demonstrates the need of a real time data visualization. Because this can not be effectively performed with the actual version of the manufacturer processing code, future work will be devoted to develop an user data acquisition, processing and visualization software.

The Quality Control monitoring of the BIOME-04 data showed that improvements are needed to increase the number of profitable casts. In fact, problems due to the presence of spikes and gaps were detected within the AC-9 absorption and attenuation data. Also, only a small fraction of BB-9 measurements have been identified as top quality data.

The Biome-04 cruise offered a valuable opportunity for a direct comparison between AC-9 and AC-S data. A complete investigation of the agreement of these two instrument can not be included in the present report, and is going to be pursued in an independent study with additional data. The analysis here presented, which mainly focused to tune the spike removal scheme, suggests that AC-9 absorption data are less accurate at the highest wavelengths than corresponding AC-S data. Also a surprisingly high correlation was found between attenuation values at different channels for both the AC-9 and the AC-S device.

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